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(54) Title: DIREACTIVE MESOGENIC COMPOUNDS AND INTERMEDIATES

(57) Abstract

The invention relates to directive mesogenic compounds or mixtures thereof comprising mesogene-containing molecule, said mesogens having two side chains attached thereto which contain a terminal polymerizable functional group, said mesogens and said functional groups being separated by at least two to twenty spacer atoms, wherein both spacer groups have different chain length.

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The invention relates to

a) treating a mesogenic diol of formula I,



MG is a mesogenic group.

$$\text{X}^2-(\text{CH}_2)_n-\text{R}^b \quad (\text{III})$$

20

X¹ and X² are each independently Cl, Br or J,

25 m and n are different integers between 1 and 20

R^a and R^b are each independently groups selected from



W is H, CH₃ or Cl.

35 in the presence of a base, and

2

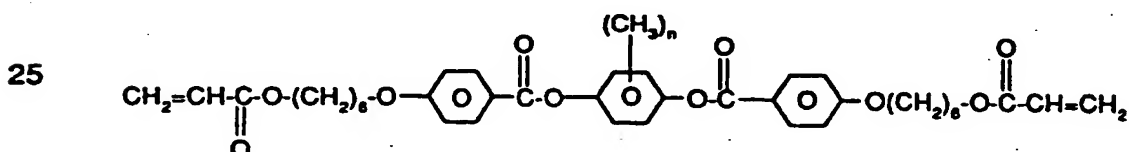
b) treating the resulting intermediate

- in the case of R^a and R^b being $-\text{CH}_2\text{OH}$, with a vinyl derivative of formula $\text{CH}_2=\text{CW}-(\text{CO})_a-\text{O}-$ or a reactive derivative thereof, in which a is 0 or 1
- in the case of R^a and R^b being $-\text{CH}=\text{CWH}$ with a perbenzoic acid.

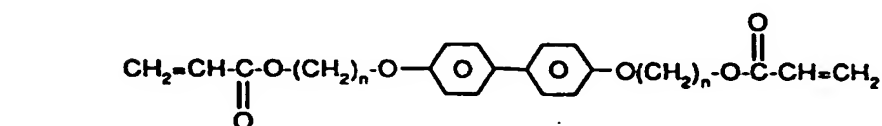
The invention furthermore relates to the preparation of such compounds and to their use in electrooptical scattering systems and for the preparation of oriented liquid crystal polymers.

Reactive liquid crystal compounds can be polymerized in situ, whilst in their liquid crystal phase, to give highly crosslinked anisotropic films which can be used, for example, as polarizing beam splitters (see, for example, EP 0,428,213). Reactive liquid crystal compounds have furthermore been proposed for electrooptical scattering systems (see, for example, EP 0,451,905), cholesteric polarizers (e.g. EP 0,606,940) and compensation films for STN displays (e.g. EP 0,423,881).

Reactive liquid crystal diesters of formula



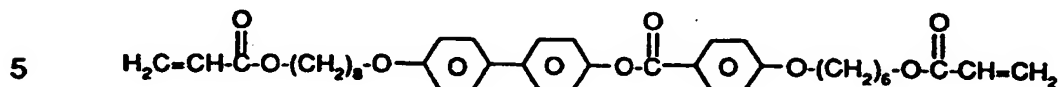
are mentioned in EP 0,261,712 ($n=0$), EP 0,331,233 ($n=1$). Reactive liquid crystal biphenyls of formula



35 are disclosed by EP 0,405,713.

3

The International Patent application WO 93/22397 discloses a compound of formula



10 These reactive liquid crystalline compounds often exhibit, however, rather high melting points disadvantageous values of the birefringence and comparable narrow mesophase ranges.

15 In view of the broad range of applications of reactive liquid crystal compounds it was desirable to have available further compounds of this type which fulfill the various requirements such as a reasonably low melting point, a high birefringence, a broad mesogenic range and preferably an enantiotropic nematic range to a high degree.

20 It was an object of the present invention to provide new reactive liquid crystalline compounds with advantageous properties thus extending the pool of reactive liquid crystal compounds available to the expert. Other objects of the present invention can be taken from the following detailed specification.

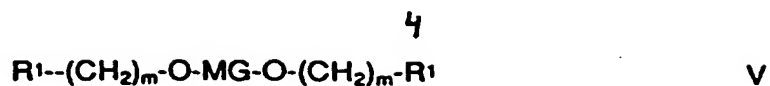
25 The present invention thus relates to reactive mesogenic compounds or mixtures thereof obtainable by treating mesogenic diols of formula I, in particular those having a symmetric structure unit with a mixture of halides of formula II and III and to their use in electrooptical systems of scattering type and for the preparation of oriented liquid crystal polymers. The invention furthermore relates to the preparation of compounds according to formula I.

30 Preferred embodiments of the present invention are:

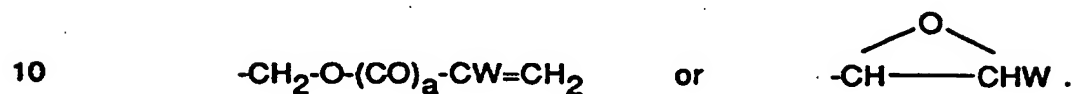
- 35 a) Composition of direactive compounds comprising at least one compound of each formula IV, V and VI,



IV



5 in which MG, m and n have the meaning given, and
 R¹ and R² are each independently



b) Direactive compound or mixture thereof

15 in which

$m - n \geq 1$, in particular 2, 3 or 4.

c) Direactive compound or mixture thereof in which

20 MG is a mesogenic group of formula VII,



25 in which

A¹ and A² are each independently

30 (a) 1,4-phenylene in which one or two CH groups may be replaced by N;

(b) 1,4-cyclohexylene in which one or two non-adjacent CH₂ groups may be replaced by -O- or one -CH- group may be replaced by -C(CN)-;

35

5

(c) naphthalene-2,6-diyl;

it being possible that group (a) is substituted by halogen
cyano or alkyl, alkoxy or alkanoyl with 1 to 6 C atoms,

5

Z¹

is each independently -COO-, -O-CO-, -CH₂-CH₂-,
-C≡C-, -CH₂O-, -OCH₂- or a single bond, and

o

is 1, 2 or 3.

10

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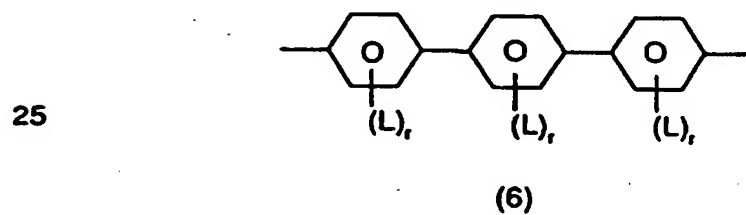
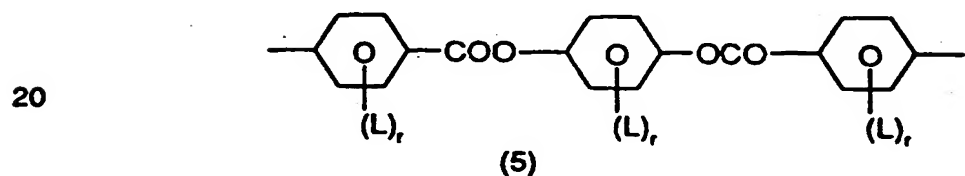
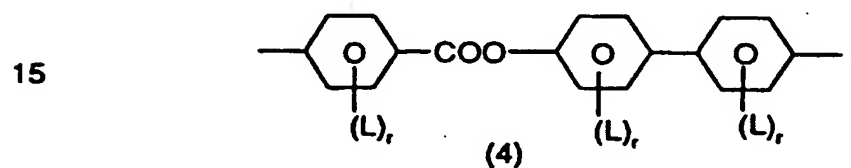
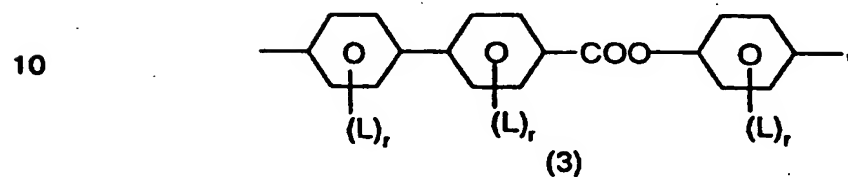
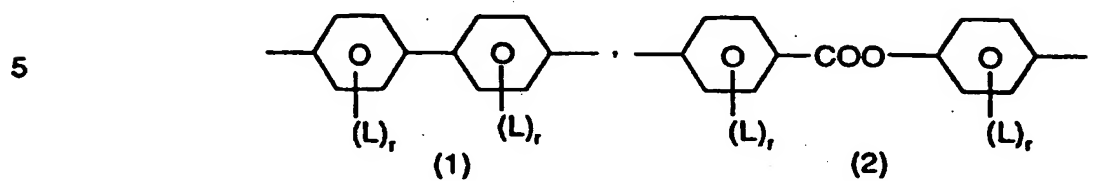
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30

35

6

- d) Direactive compound or mixture thereof in which MG is selected from the structure elements (1) to (6).



in which

30

L is CH₃, Cl, F, OCH₃ or -CO-CH₃, and

r is 0, 1, 2 or 4.

35

7

e) Direactive compound or mixture thereof in which

n and m are given by the following table:

5	m	5	5	5	4	4
	n	2	3	4	2	3

A further aspect of the present invention are direactive compounds of formula IV A



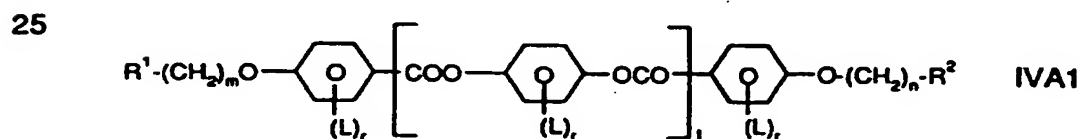
in which

15 R^1 and R^2 have the meaning given,

m and n are different integers between 2 and 10, and

20 MG is a mesogenic group, the core of which being symmetrical, preferably a structure element of formula (1), (5) or (6), in particular

direactive compounds of the formula IVA1



30 in which

R^1 , R^2 ,
L and r have the meaning given,

35

8

m and n are different integers between 2 and 10, and

t is 0 or 1.

5 Another aspect of the invention are the polymers prepared by polymerizing a monomer according to any of the preceding claims and

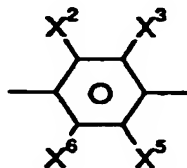
10 a chemical intermediate compounds or mixtures thereof useful in preparing reactive compounds or mixtures thereof according to any of the claim 1 to 8, comprising mesogene-containing molecules, said mesogenes having two side chains attached thereto that contain hydroxyl or vinyl group at the end thereof, said mesogenes and said functional groups being separated by at least two to twenty spacer atoms, wherein both spacer groups have different chain length.

15

Above and below, the term reactive mesogenic compounds refers to reactive rod-like molecules which may be enantiotropic, monotropic or isotropic, preferably, however, enantiotropic or monotropic.

20 In the inventive compounds in which MG is a mesogenic group of formula VIII, A¹ and A² can be independently from each other an unsubstituted or a substituted 1,4-phenylene group of formula

25



30

X², X³, X⁵ and X⁶ can be independently from each other H, F, Cl, methyl or CN.

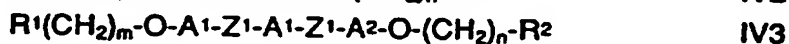
In the following, for the sake of simplicity, the following notation will be used:

35

9

Phe. 2 X² 3 X³ 5 X⁵ 6 X⁶ is a 1,4-phenylene group carrying in 2-position the group X², in 3-position the group X³ etc.; in case X², X³, X⁵ and/or X⁶, denote H, this will not be specified in above notation, i.e. only true substitutions will be listed. Thus Phe, for example, is an unsubstituted 1,4-phenylene group while Phe.2F 5 Cl is a 2-fluoro-5-chloro-1,4-phenylene group. Furthermore, Pyr is pyrimidine-2,5-diyl, Pyd is pyridine -2,5-diyl and Nap is a naphthalene-2,6-diyl group. The notation Pyr and Pyd in each case include the 2 possible positional isomers.

The compounds according to formula IV comprise 2- and 3-ring compounds (n=1 or 2) of formula IV2 and IV3:



In the 3-ring compounds of formula IV3, the ring groups A¹ can be chosen independently from each other.

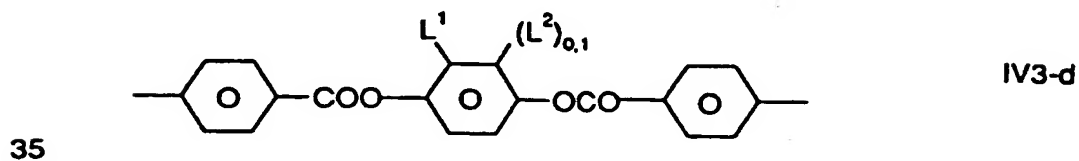
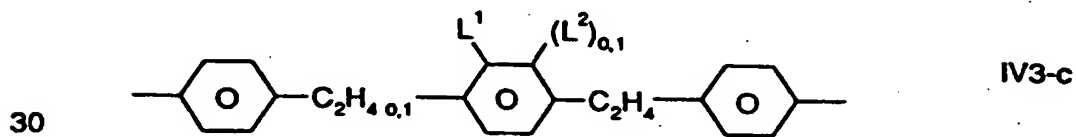
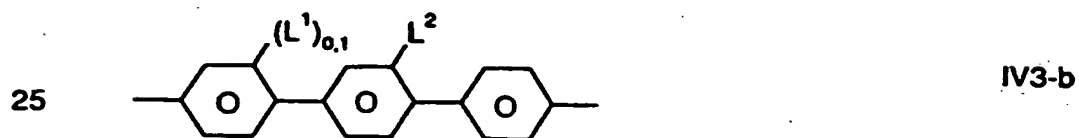
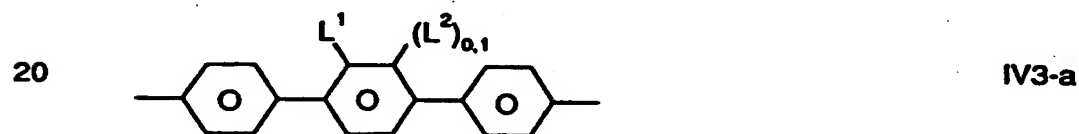
Especially preferred is a smaller group of 2-ring compounds exhibiting the following structures for -A¹-Z¹-A²-:

	-Phe.2CH ₃ -Phe-	IV2-1
	-Phe.3CH ₃ -Phe-	IV2-2
	-Phe.2Cl-Phe-	IV2-3
25	-Phe.3Cl-Phe-	IV2-4
	-Phe.2CN-Phe-	IV2-5
	-Phe.3CN-Phe-	IV2-6
	-Phe.2Cl3Cl-Phe-	IV2-7
	-Phe.2Cl3F-Phe-	IV2-8
30	-Phe.2F-Phe-	IV2-9
	-Phe.3F-Phe-	IV2-10
	-Phe.-Phe-	IV2-11
	-Phe.F-Nap-	IV2-12
35	-Phe.2Cl-Nap-	IV2-13

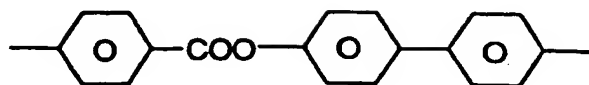
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5	-Phe.F-Nap- -Phe.3Cl-Nap- -Phe.2F-Pyr- -Phe.2F-Pyr- -Phe.2CH ₃ -Pyd- -Phe.2Cl-Pyd-	IV2-14 IV2-15 IV2-16 IV2-17 IV2-18 IV2-19
10	-Phe.F-CH ₂ CH ₂ -Phe- -Phe.3F-CH ₂ CH ₂ -Phe- -Phe.2Cl-CH ₂ CH ₂ -Phe- -Phe.3Cl-CH ₂ CH ₂ -Phe- -Phe.2CN-CH ₂ CH ₂ -Phe- -Phe.3CN-CH ₂ CH ₂ -Phe- -Phe.2Cl3Cl-CH ₂ CH ₂ -Phe- -Phe.2Cl3F-CH ₂ CH ₂ -Phe-	IV2-20 IV2-21 IV2-22 IV2-23 IV2-24 IV2-25 IV2-26 IV2-27
15		

The 3-ring compounds according to formula IV3 preferably exhibit the following structures for -A¹-Z¹-A¹-Z¹-A²:



II



IV3-e

5

In these structures, IV3-a to IV3-d, L¹ and L² denote independently from each other H, -Cl, -F, -CN and C₁H₂₋₁₋₃ and , in particular, -Cl, -F, -CN, -CH₃, and/or -C₂H₅.

10

Especially preferred are the following patterns:

15	-Phe-Phe.2CH ₃ -Phe-	IV3-a-1
	-Phe-Phe.2Cl-Phe-	IV3-a-2
	-Phe-Phe.2CN-Phe-	IV3-a-3
	-Phe-Phe.2F-Phe-	IV3-a-4
	-Phe-Phe-Phe-	IV3-a-5
	-Phe-Phe.2C ₂ H ₅ -Phe-	IV3-a-6
20	-Phe-Phe.3CH ₃ -Phe-	IV3-b-1
	-Phe-Phe.3Cl-Phe-	IV3-b-2
	-Phe-Phe.3CN-Phe-	IV3-b-3
	-Phe-Phe.3F-Phe-	IV3-b-4
	-Phe-Phe.3C ₂ H ₅ -Phe-	IV3-b-5
25	-Phe.3F-Phe.3Cl-Phe-	IV3-b-6
	-Phe.3F-Phe.3CH ₃ -Phe-	IV3-b-7
	-Phe.3Cl-Phe.3Cl-Phe-	IV3-b-8
	-Phe.3Cl-Phe.3CH ₃ -Phe-	IV3-b-9
	-Phe-Phe.2Cl-Phe.3Cl-	IV3-b-10
30	-Phe-Phe.3Cl-Phe.3Cl-	IV3-b-11
	-Phe-Phe.2Cl-Phe.2Cl-	IV3-b-12
	-Phe-Phe.3Cl-Phe.2Cl-	IV3-b-13
	-Phe-Phe.2CH ₃ -Phe.3Cl-	IV3-b-14
	-Phe-Phe.3CH ₃ -Phe.3Cl-	IV3-b-15
35	-Phe-Phe.2CH ₃ -Phe.2Cl-	IV3-b-16

	-Phe-Phe.3CH ₃ -Phe.2Cl-	IV3-b-17
	-Phe-Phe.2F-Phe.3Cl-	IV3-b-18
	-Phe-Phe.3F-Phe.3Cl-	IV3-b-19
	-Phe-Phe.2F-Phe.2Cl-	IV3-b-20
5	-Phe-Phe.3F-Phe.2Cl-	IV3-b-21
	-Phe-Phe.2Cl-Phe.3CN-	IV3-b-22
	-Phe-Phe.3Cl-Phe.3CN-	IV3-b-23
	-Phe-Phe.2Cl-Phe.2CN-	IV3-b-24
	-Phe-Phe.3Cl-Phe.2CN-	IV3-b-25
10	-Phe-Phe.2CH ₃ -Phe.3CN-	IV3-b-26
	-Phe-Phe.3CH ₃ -Phe.3CN-	IV3-b-27
	-Phe-Phe.2CH ₃ -Phe.2CN-	IV3-b-28
	-Phe-Phe.3CH ₃ -Phe.2CN-	IV3-b-29
	-Phe-Phe.3F-Phe.3CN-	IV3-b-30
15	-Phe-Phe.2F-Phe.3CN-	IV3-b-31
	-Phe-Phe.3F-Phe.2CN-	IV3-b-32
	-Phe-Phe.2F-Phe.2CN-	IV3-b-33
	-Phe-Phe.2F-Phe.2F-	IV3-b-34
	-Phe-Phe.3F-Phe.3F-	IV3-b-35
20		
	-Phe-Phe.2CH ₃ -C ₂ H ₄ -Phe-	IV3-c-1
	-Phe-Phe.2Cl-C ₂ H ₄ -Phe-	IV3-c-2
	-Phe-Phe.2CN-C ₂ H ₄ -Phe-	IV3-c-3
	-Phe-Phe.2F-C ₂ H ₄ -Phe-	IV3-c-4
25	-Phe-Phe.2C ₂ H ₅ -C ₂ H ₄ -Phe-	IV3-c-5
	-Phe-Phe.2Cl3F-C ₂ H ₄ -Phe-	IV3-c-6
	-Phe-Phe.2Cl3Cl-C ₂ H ₄ -Phe-	IV3-c-7
	-Phe-C ₂ H ₄ -Phe.2CH ₃ -C ₂ H ₄ -Phe-	IV3-c-8
	-Phe-C ₂ H ₄ -Phe.2Cl-C ₂ H ₄ -Phe-	IV3-c-9
30	-Phe-C ₂ H ₄ -Phe.2CN-C ₂ H ₄ -Phe-	IV3-c-10
	-Phe-C ₂ H ₄ -Phe.F-C ₂ H ₄ -Phe-	IV3-c-11
	-Phe-C ₂ H ₄ -Phe.2OCF ₃ -C ₂ H ₄ -Phe-	IV3-c-12
35		
	-Phe-COO-Phe.OCO-Phe-	IV3-d-1
	-Phe-COO-Phe.2CH ₃ -OCO-Phe-	IV3-d-2

13

5	-Phe-COO-Phe.3CH ₃ -OCO-Phe-	IV3-d-3
	-Phe-COO-Phe.2CH ₃ 3CH ₃ -OCO-Phe-	IV3-d-4
	-Phe-COO-Phe.2OCH ₃ -OCO-Phe-	IV3-d-5
	-Phe-COO-Phe.2Cl-OCO-Phe-	IV3-d-6
	-Phe-COO-Phe.2F-OCO-Phe-	IV3-d-7
	-Phe-COO-Phe.2F3F-OCO-Phe-	IV3-d-8
10	-Phe-COO-PhePhe-	IV3-e-1
	-Phe-COO-Phe.2FPhe-	IV3-e-2
	-Phe-COO-Phe.3FPhe-	IV3-e-3
	-Phe-COO-PhePhe.2F-	IV3-e-4
	-Phe-COO-PhePhe.3F-	IV3-e-5
	-Phe.2F-COO-PhePhe-	IV3-e-6
15	-Phe.3F-COO-PhePhe-	IV3-e-7

It was observed that the stability of 3-ring compounds wherein one of the 2 groups Z¹ is -COO- or -OCO- while the other denotes a single bond, can be increased if the compound is laterally di- or higher substituted, particularly di-substituted by -Cl, -F, -CN and/or -CH₃. Compounds of this type are preferred.

Especially preferred are further 3-ring compounds where both groups Z¹ are either -COO-, or -OCO- and at least one of the rings A¹, A^{1'} and A² are at least mono substituted.

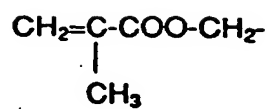
In the compounds of formula IV R¹ is CH₂ = CW-COO-CH₂-, CH₂ =

CH-O-CH₂-, $\text{HW}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{C}-$, with W being H, Cl or alkyl with 1-5 C atoms and m being 1-7.

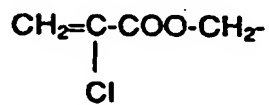
Preferably, R¹ and R² is a vinyl group, an acrylate group, an epoxy group and especially preferred are the following means of R¹ and R²:

CH₂=CH-COO-CH₂- R¹-1

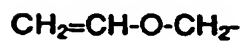
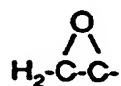
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R¹-2.

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R¹-3

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R¹-4R¹-5

with alkyl denoting C₁-C₃-alkyl and m being 1-5.

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The reaction methods mentioned are briefly summarized in the following synthetic tree:

Scheme I

5

HO-MG-OH

10

+
Mixture of
 $\text{Br}-(\text{CH}_2)_m-\text{OH}$ /
 $\text{Br}-(\text{CH}_2)_n-\text{OH}$
Butanone, K_2CO_3 , heat

15

$\text{HO}-(\text{CH}_2)_m \text{O-MG-O}-(\text{CH}_2)_m-\text{OH}$
 $\text{HO}-(\text{CH}_2)_m \text{O-MG-O}-(\text{CH}_2)_n-\text{OH}$
 $\text{HO}-(\text{CH}_2)_n \text{O-MG-O}-(\text{CH}_2)_n-\text{OH}$

Mixture

20

Butylvinyl ether
DCM
1,10-Phenanthroline
Pd (II)-Acetate

 $\text{CH}_2 = \text{CW-COCl}$

Mixture of
"diacrylates"

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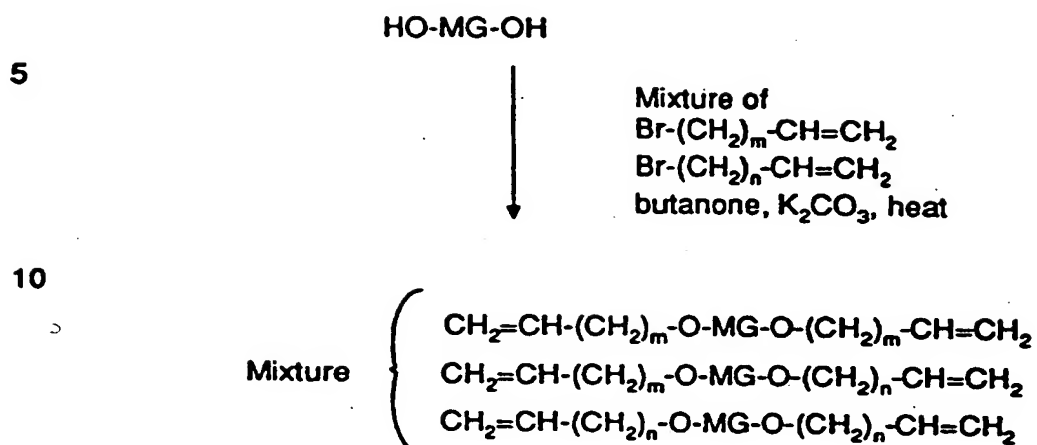
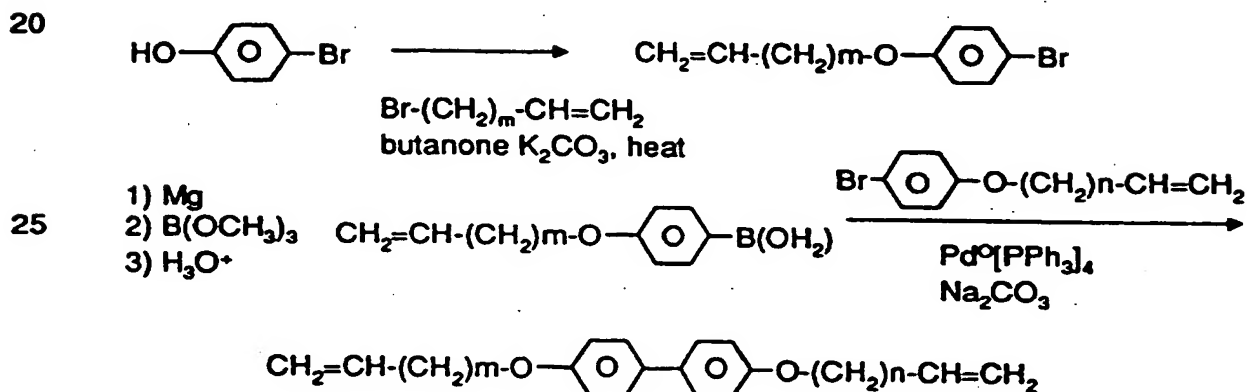
Mixture of
"Divinylethers"

DCM = dichloromethane

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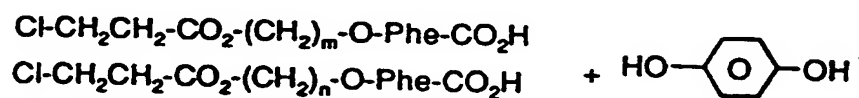
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Scheme IIScheme III

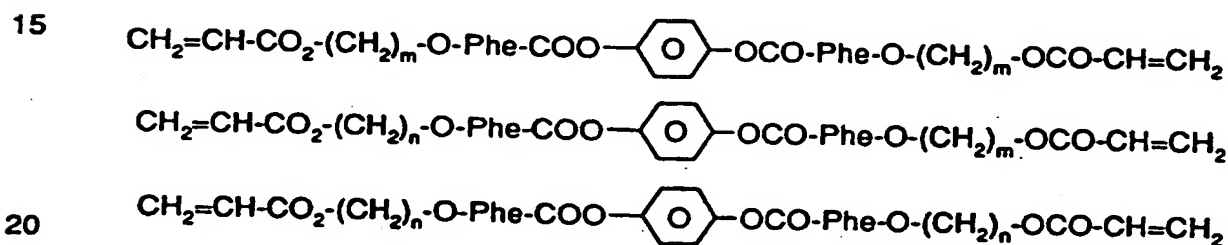
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Certain compounds or mixtures according to the invention are obtainable in a "one-pot-synthesis" as outlined in scheme IV:

5 Scheme IV



1) TFAA/DCM
 2) TEA/DCM



TFAA = trifluoroacetic acid
 TEA = triethylamine

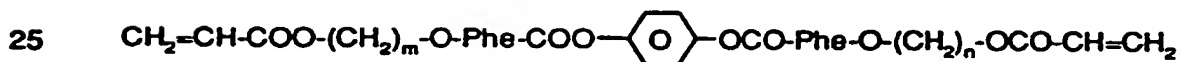
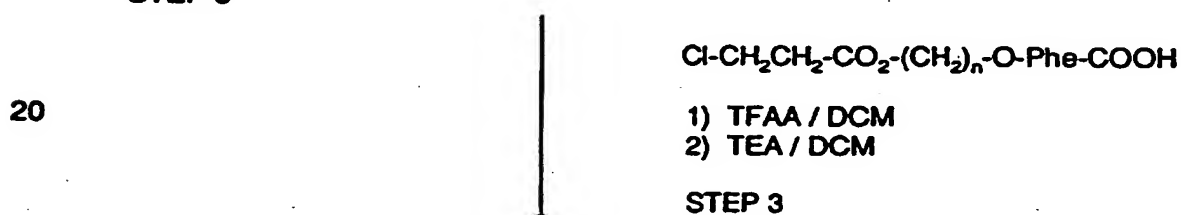
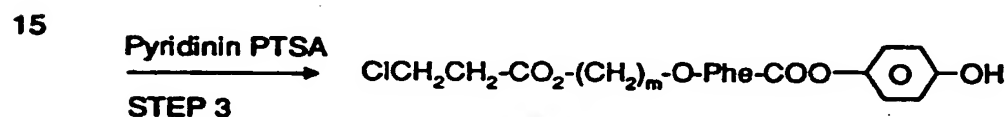
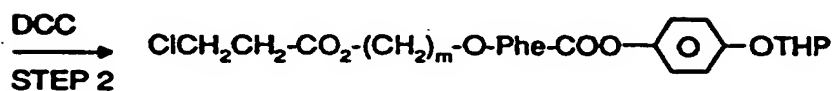
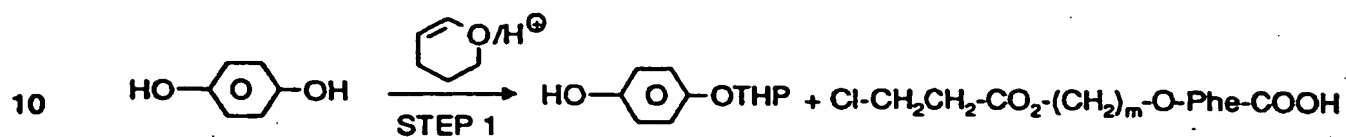
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Individual compounds of this type can be obtained according to schemes V to VII:

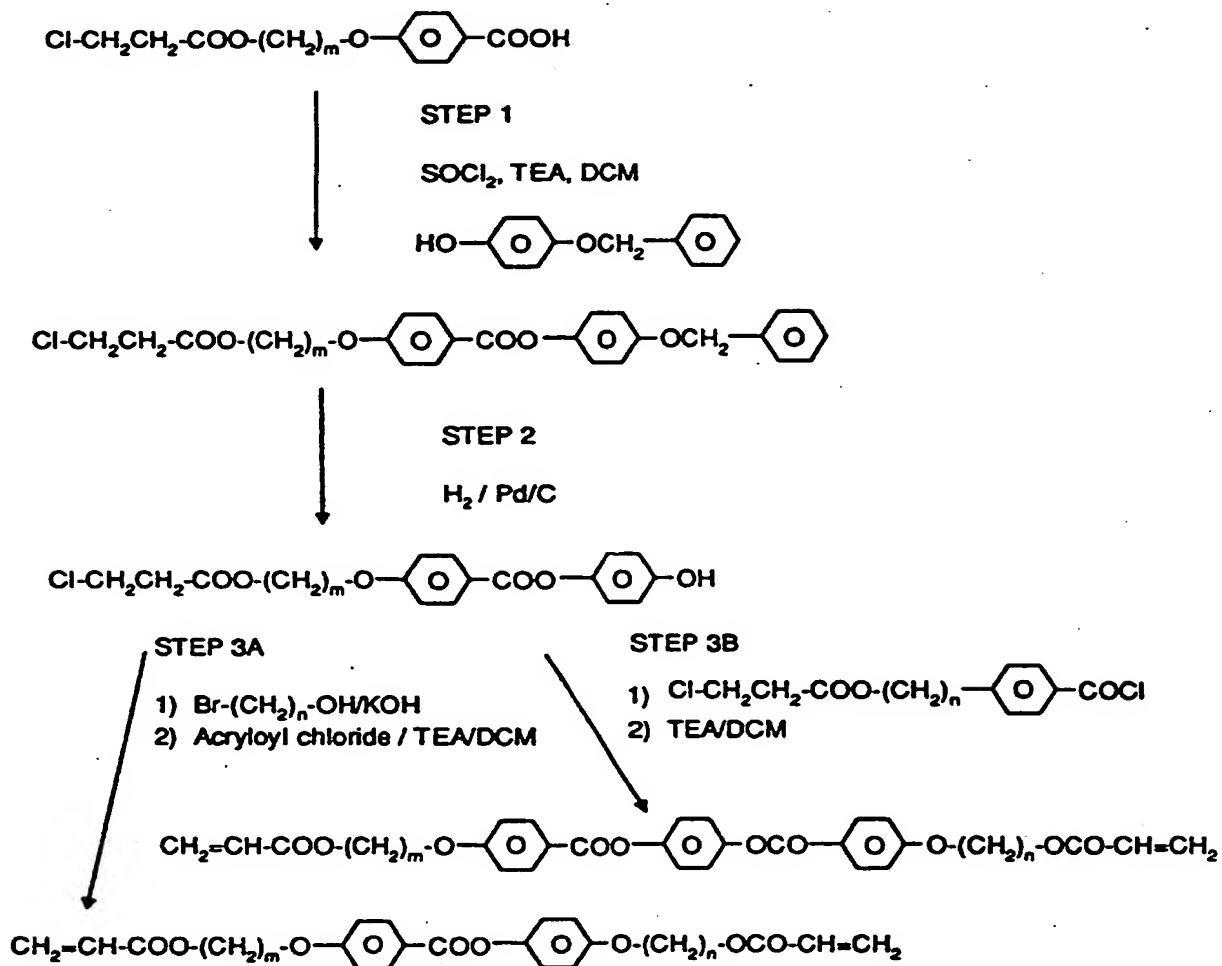
5 Scheme V

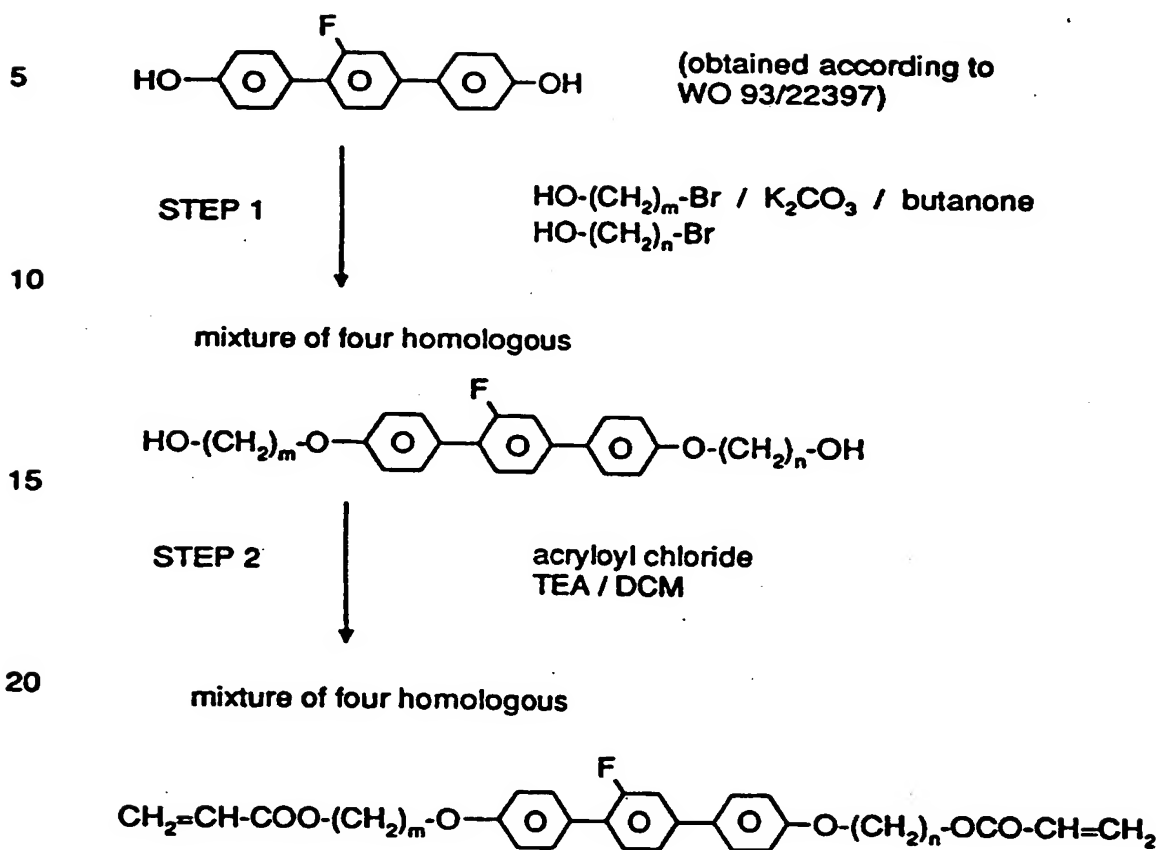


PTSA = p-toluenesulfonate

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Scheme VI

Scheme VII

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The reaction schemes mentioned above are to illustrate the invention without restricting it. The expert can choose other reaction methods without any inventive efforts.

5 In the following and in the preceding, all percentages given are percentages by weight. Temperatures are given in degrees Celsius.

The following examples are intended to illustrate the invention without restricting it.

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Example 1

The reactive liquid crystalline compound (1)

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is prepared via the sequence of reaction steps shown in scheme V. In step 4 of scheme V 2.2 moles TFAA are added dropwise to a solution 2 moles of the phenol obtained in step 3 of scheme V and 2 moles of the benzoic acid in 2 l of DCM.

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The reaction mixture is stirred at room temperature for 16 hours. Then 5 moles of TEA in 1 l of DCM are added. The mixture is stirred for 16 hours. Aqueous work-up and column chromatography give (1) which shows K 111 S.

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The following compounds are obtained analogously:


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Compound No.	m	n	phase transition temperatures (°C)
(2)	3	5	K 76 N 160 I
(3)	4	5	K 67 N 165 I
(4)	4	6	K 78 S 82 N 159 I
(5)	5	6	K 78 S 80 N 162 I
Comp 1	4	4	K 105 N 164 I
Comp 2	5	5	K 91 N 167 I
Comp 3	6	6	K 105 (S 95) 152 I

Example 2

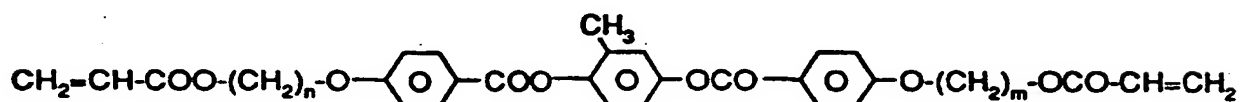
A mixture of 1 mol $\text{Cl-CH}_2\text{CH}_2\text{-COO-(CH}_2)_4\text{-O-}$  -COOH ,

1 mol $\text{Cl-CH}_2\text{CH}_2\text{-COO-(CH}_2)_4\text{-O-}$  -COOH , and 1 mol

p-hydroquinone is treated with 22 moles of TFAA followed by 2.5 moles of TEA.

A mixture consisting of 1 part comp 1 and 1 part comp 3 and 2 parts of Compound No. (4) is obtained which shows a melting point of 56 °C and a clearing point of 163 °C.

Analogously a mixture of the following compounds is obtained:



n	m	parts
3	3	1
6	6	1
3	6	1
6	3	1

This composition shows a melting point below 30 °C and a clearing point of 119 °C.

Example 3

A mixture of 0.5 moles of biphenol, 1.3 moles of potassium hydroxide, 0.6 moles of 3-bromopropanol and 0.6 moles of 3 bromohexanol is heated in 2 litres of butanone for 16 hrs. After aqueous work-up a mixture of

1 part of $\text{HO}-(\text{CH}_2)_3-\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{O}-(\text{CH}_2)_3-\text{OH}$

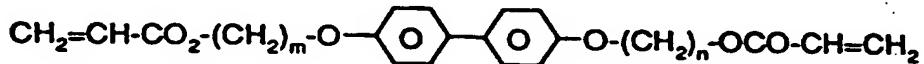
1 part of $\text{HO}-(\text{CH}_2)_6-\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{O}-(\text{CH}_2)_6-\text{OH}$, and

2 parts of $\text{HO}-(\text{CH}_2)_6-\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{O}-(\text{CH}_2)_3-\text{OH}$

is obtained.

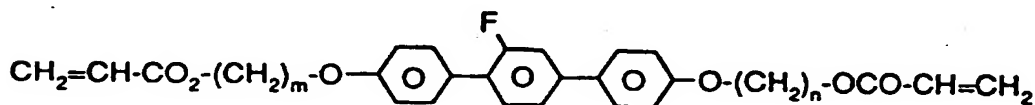
This mixture is treated with 1.2 moles of acryloyl chloride and 1.2 moles of TEA in 1.5 litres of dichloroethane DCM and refluxed for 3 hours.

After aqueous work-up the resulting reaction mixture is purified by column-chromatography to yield a mixture of diacrylates (6), (7) and (8).



Compound No.	m	n	parts
(6)	3	3	1
(7)	5	6	1
(8)	3	6	2

Analogously a mixture of compounds of formulae (9), (10), (11) and (12) is obtained



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	Compound No.	m	n	parts
	(9)	3	3	1
	(10)	6	6	1
5	(11)	3	6	1
	(12)	6	3	1

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Claims

1. Direactive mesogenic compounds or mixtures thereof obtainable by

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- a) treating a mesogenic diol of formula I,



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in which

MG is a mesogenic group,

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with a mixture of the halids of formula II and III,



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in which

X¹ and X² are each independently Cl, Br or J,

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m and n are different integers between 1 and 20

R^a and R^b are each independently groups selected from



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wherein

W is H, CH₃ or Cl,

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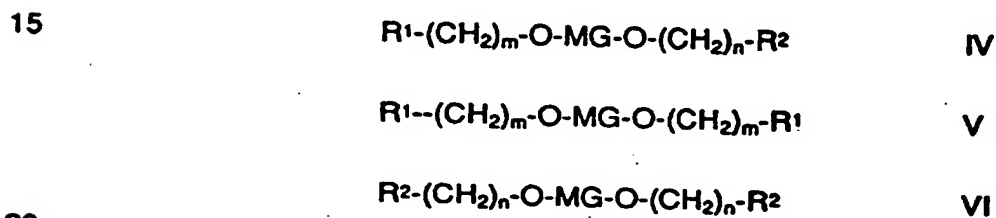
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in the presence of a base, and

b) treating the resulting intermediate

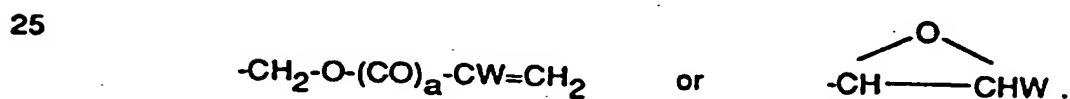
- 5
- in the case of R^a and R^b being $-\text{CH}_2\text{OH}$, with a vinyl derivative of formula $\text{CH}_2=\text{CW}-(\text{CO})_a-\text{O}-$ or a reactive derivative thereof, in which a is 0 or 1
 - 10 - in the case of R^a and R^b being $-\text{CH}=\text{CWH}$ with a perbenzoic acid.

2. Composition of direactive compounds comprising at least one compound of each formula IV, V and VI,



in which MG, m and n have the meaning given, and

R^1 and R^2 are each independently



3. Direactive compound or mixture thereof according to claim 1 or 2

30 in which

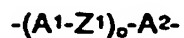
$$m - n \geq 1.$$

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4. Direactive compound or mixture thereof according to any of the preceding claim in which

MG is a mesogenic group of formula VII,



VIII

in which

A¹ and A² are each independently

(a) 1,4-phenylene in which one or two CH groups may be replaced by N;

(b) 1,4-cyclohexylene in which one or two non-adjacent CH₂ groups may be replaced by -O- or one -CH- group may be replaced by -C(CN)-;

(c) naphthalene-2,6-diyl;

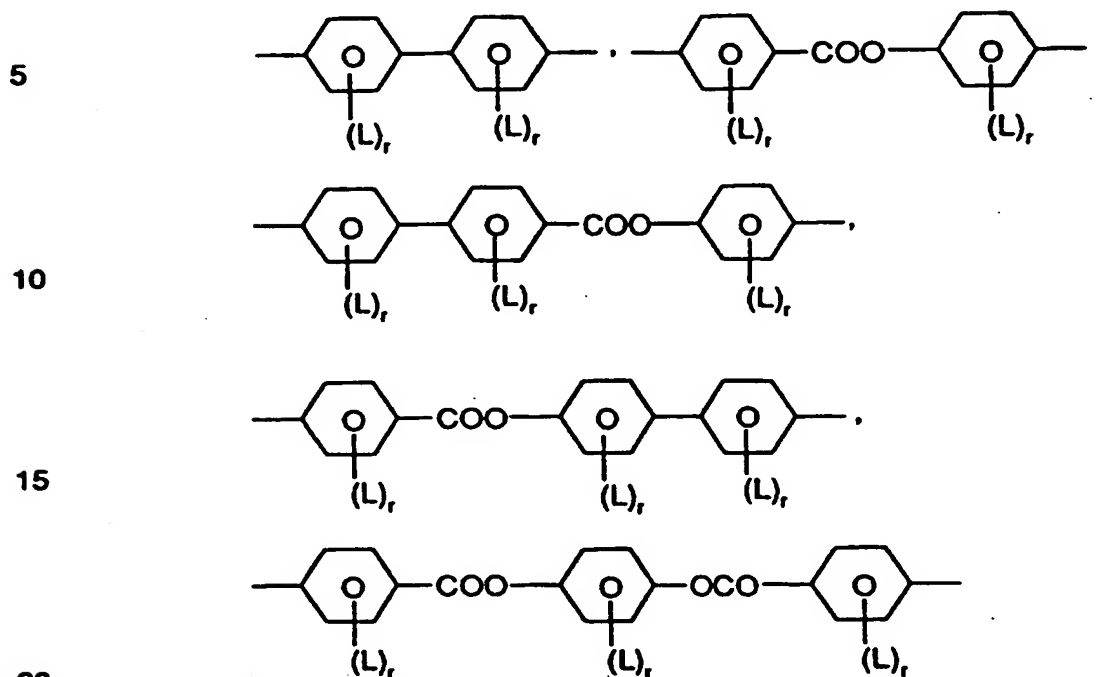
it being possible that group (a) is substituted by halogen cyano or alkyl with 1 to 6 C atoms,

Z¹ is each independently -COO-, -O-CO-, -CH₂-CH₂-, -C≡C-, -CH₂O-, -OCH₂- or a single bond, and

o is 1, 2 or 3.

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5. Direactive compound or mixture thereof according to any of the preceding claims in which MG is selected from



in which

L is CH_3 , Cl, F, OCH_3 or $-\text{CO}-\text{CH}_3$, and

r is 0, 1, 2 or 4.

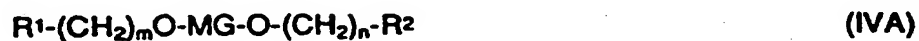
6. Direactive compound or mixture thereof according to any of the preceding claims in which

n and m are given by the following table:

m	5	5	5	4	4
n	2	3	4	2	3

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7. Direactive compound of formula IV A



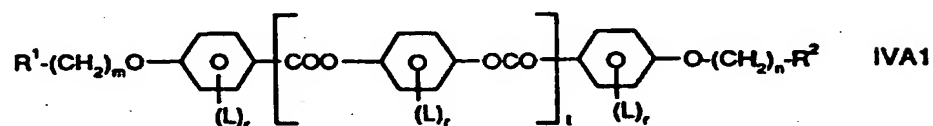
in which

R^1 and R^2 have the meaning given,

m and n are different integers between 2 and 10, and

MG is a mesogenic group, the core of which being symmetrical.

8. Direactive compound according to claim 7 of the formula IVA1



in which

R^1 , R^2 ,
 L and r have the meaning given,

m and n are different integers between 2 and 10, and

t is 0 or 1.

9. Polymers prepared by polymerizing a monomer according to any of the preceding claims.

10. Chemical intermediate compounds or mixtures thereof useful in preparing direactive compounds or mixtures thereof according to any of the claim 1 to 8, comprising mesogene-containing molecules, said mesogenes having two side chains attached thereto

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that contain hydroxyl or vinyl group at the end thereof, said mesogenes and said functional groups being separated by at least two to twenty spacer atoms, wherein both spacer groups have different chain length.

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INTERNATIONAL SEARCH REPORT

International Application No.
P.1/EP 96/00240

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09K19/20 C09K19/12 C07C43/23 C07C69/92 C08F20/10
C09K19/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09K C07C C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,93 22397 (MERCK PATENT GMBH) 11 November 1993 cited in the application see the whole document and particularly example 4.1	1-10
X	GB,A,2 280 445 (MERCK PATENT GMBH) 1 February 1995 see claims 1-15	1-9
Y	EP,A,0 261 712 (N.V. PHILIPS' GLOEILAMPENFABRIKEN) 30 March 1988 cited in the application see the whole document	1-9
	-/--	

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Date of the actual completion of the international search

21 May 1996

Date of mailing of the international search report

30-05-1996

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Beslier, L

INTERNATIONAL SEARCH REPORT

Inventor's Application No
PCT/EP 96/00240

C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 405 713 (EDISON POLYMER INNOVATION CORP.) 2 January 1991 cited in the application see the whole document ---	1-10
Y	EP,A,0 331 233 (N.V. PHILIPS' GLOEILAMPENFABRIEKEN) 6 September 1989 cited in the application see the whole document ---	1-9
Y	DE,A,42 26 994 (SIEMENS AG) 17 February 1994 see the whole document ---	1-9
Y	EP,A,0 611 981 (F. HOFFMANN-LA ROCHE AG) 24 August 1994 see the whole document ---	1-9
P,Y	EP,A,0 648 827 (MERCK PATENT GMBH) 19 April 1995 see the whole document ---	1-10
P,X	WO,A,95 22586 (BASF AG) 24 August 1995 see the whole document ---	1-10
P,X	WO,A,95 24454 (BASF AG) 14 September 1995 see the whole document ---	1-10
P,X	WO,A,95 24455 (BASF AG) 14 September 1995 see the whole document ---	1-9
E	WO,A,96 04351 (BASF AG) 15 February 1996 see example 4 -----	1-9

INTERNATIONAL SEARCH REPORT

Information on patent family members

Patent Application No

96/00240

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9322397	11-11-93	EP-A- 0591508 JP-T- 6507987	04-94 09-94
GB-A-2280445	01-02-95	JP-A- 7053961	28-05-95
EP-A-261712	30-03-88	JP-B- 8003586 JP-A- 63064029 US-A- 4892392	17-01-88 22-03-88 09-01-90
EP-A-405713	02-01-91	US-A- 5078910 CA-A- 2014966 JP-A- 3041043	07-01-92 20-12-90 21-02-91
EP-A-331233	06-09-89	NL-A- 8802832 JP-A- 2006927 US-A- 4983479	18-09-89 11-01-90 08-01-91
DE-A-4226994	17-02-94	NONE	
EP-A-611981	24-08-94	CN-A- 1096807 CN-A- 1091458 EP-A- 0611786 JP-A- 6289374 JP-A- 6287453	28-12-94 31-08-94 24-08-94 18-10-94 11-10-94
EP-A-648827	19-04-95	NONE	
WO-A-9522586	24-08-95	DE-A- 4405316	24-08-95
WO-A-9524454	14-09-95	DE-A- 4408171	14-09-95
WO-A-9524455	14-09-95	DE-A- 4408170	14-09-95
WO-A-9604351	15-02-96	DE-A- 4427766	08-02-96

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